NITROGEN TETROXIDE PROPELLANT FOR SPACE ENGINE APPLICATIONS

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Special Report (technical)
Nitrogen Tetroxide Propellant for Space Engine Applications

INTRODUCTION

The substance nitrogen tetroxide (NTO), N_2O_4, is a material which is widely used as an oxidizer in liquid rocket engine systems because it is cheap and a relatively high-energy companion to amine-type fuels. Accordingly, a number of rocket engines are being developed and produced for NASA under the Gemini and Apollo programs using material procured in accordance with military specification, MIL-P-26539A of 5 April 1963, and supplied to the contractor as Government-Furnished Propellant. This NTO is obtained from the Pinol, California and Hopewell, Virginia plants of Hercules Powder Co. and Allied Chemical Co., respectively, and inspected and accepted there in procedures outlined in the above specification.

Recently, there have been cases reported in which the nitrogen tetroxide available for engine testing at a contractor's plant was considered unsatisfactory for further use either because of a low assay or because of the presence of an unusual green color therein.

In response to a request from NASA Headquarters personnel, visits were made to the Rocket Propulsion Laboratory, Edwards Air Force Base, California and to Rocketdyne Division of North American Aviation, Inc., Canoga Park and Santa Susanna, California, in order to determine from cognizant individuals there the pertinent details of the nitrogen tetroxide logistics and the reasons for the off-quality materials.

Individuals contacted were:

Mr. A. H. Lambert - RPL
Mr. H. Malone - RPL
Mr. R. Biggers - RPL
Dr. B. Tuffly - Rocketdyne
Mr. D. Gibson - Rocketdyne
Mr. N. A. Gould - USAF Quality Assurance Representative at Rocketdyne

CHEMISTRY OF NITROGEN TETROXIDE

The oxidizer, N_2O_4, can be produced either by oxidation of ammonia (NH_3) or of nitrosyl chloride, NOCl. According to the process used, there will be significantly different contaminants present and consequently pronounced differences in behavior.

Nitrogen tetroxide exists as a mixture with its monomer, nitrogen dioxide, in accordance with the following temperature-dependent equilibrium reaction, which is one of the fastest chemical reactions known:

$$N_2O_4 \rightleftharpoons 2NO_2$$

N_2O_4	$2NO_2$
Colorless	Black
100% concentration at -9°F	100% concentration at 140°F

Between the temperature limits, -9°F to 140°F therefore, the propellant color can vary such that the normal color of propellant at 70°F, where an 85% concentration of N_2O_4 obtains, is a deep reddish-brown.

The compound nitric oxide (NO), which in the neat form is colorless, can react readily with nitrogen tetroxide to form nitrogen trioxide in accordance with the following equilibrium:

$$N_2O_4 + 2NO \rightleftharpoons 2N_2O_3$$

$N_2O_4 + 2NO$	$2N_2O_3$
Brown	Blue-green

The nitrogen trioxide content is bluish green at low temperature, darkening with increasing temperatures to a deep green at increased concentration; for example, the color of propellant NTO at room temperature containing 0.5% NO is a greenish brown.

In the presence of relatively small amounts of water (about 0.1 to 0.2%), a brownish green color can also be seen with NTO. This is a consequence of the following series of reactions, whereby

N_2O_3 is produced in situ:

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$$
$$HNO_2 \longrightarrow N_2O_3 + \tfrac{1}{2}H_2O$$

Green

Thus it can be seen that the green color in propellant NTO can be due either to the presence of moisture or to nitric oxide. As will be shown later herein, the presence of small amounts of NO is not necessarily deleterious; the presence and amounts of water above the specification limit, however, can be disastrous since such denotes the presence of nitric acid, a well known source of corrosion. It was for this reason that the appearance of "green" NTO from Hercules, presumably from a new process, when first noticed caused a great deal of alarm. Only when chemical analysis proved the absence of large amounts of water therein and after a great deal of research could the material be used for further work.

ANALYSIS OF NITROGEN TETROXIDE

Although the procedures used in MIL-P-26539A for analysis of the basic ingredients are widely used, they are now under severe criticism from propellant chemists at several contractors plants.

The procurement specification for nitrogen tetroxide, MIL-P-26539A, imposes limits on the following critical ingredients:

Nitrogen Tetroxide assay (N_2O_4)	99.5 maximum
Water equivalent	0.1 maximum

In essence, the nitrogen tetroxide content is determined by direct titration with standard sodium hydroxide, according to the equation, $N_2O_4 + 2NaOH \longrightarrow NaNO_3 + NaNO_2 + H_2O$. The water content is measured in a separate determination as a water-equivalent since moisture reacts with N_2O_4 according to the equation $N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$; the excess N_2O_4 content is distilled from the sample flask and the nitric acid left behind in the container is computed as the water-equivalent.

By their nature, the analytical determinations of the NTO and moisture content can be laborious and sometimes require up to 12 hours' time to complete.

For purposes of RPL, however, these specification methods were always used. But in order to have the benefit of a more rapid analysis for guidance of the test stand operation, Rocketdyne has developed the so-called Go-No Go method to determine the water content of propellant NTO. While presumably not as accurate as the specification method, the Go-No Go method was extremely useful in that it provided the test engineers with a rapid way of checking propellants to be used shortly thereafter in a test stand firing. It was not considered a substitute for final check-out by specification procedures to satisfy contract requirements since in all cases, test NTO was run later through the standard analytic steps for NTO and water content. The reason a rapid analysis is so essential is that the Rocketdyne subcontract from McDonnell states that propellant tested under the Gemini program must be analyzed a minimum of once a week and also when the stand tanks are filled and a firing conducted.

The Go-No Go method is based upon the color of the NTO. If water above the specification limit of 0.15% is present, there will be a green color observed; below this level the color is brown. Thus, by maintaining a series of calibration standards, with variations in the known water content, a ready comparison can be made with sufficient accuracy for the needs of the test stand engineers. Measurements are then carried out by the standard specification techniques. There have been a number of such tests made, and a comparison of typical Rocketdyne experiments follow:

<u>Specification Method</u>

Run	NTO Computation	Water-Equivalent Computation	Go-No Go Results
	%	%	
1	99.5	0.24	No Go
2	103.0	0.07	"
3	98.9	4.7	"
4	99.3	6.20	"
5	99.3	0.10	"
6	99.5	0.10	Marginal
7	99.1	0.17	No Go

The striking point about this listing is the appearance of a 103.0% number in Run 2 which appeared at Reno on production engine testing. This result is not a mistake in computation but reflects a basic defect of MIL-P-26539A, in that the N_2O_4 analysis is not specific for that substance. Since the N_2O_4 content is determined by reaction with so many equivalents of sodium hydroxide, any acidic materials contained therein, such as HNO_3 or NO, which also consume sodium hydroxide will in turn be calculated as N_2O_4; however, the computations based on theoretical equivalent weight will be badly in error. The following table, which is based upon a theoretical titration of NTO with known water content illustrates this point.

N_2O_4 really present	Water if combined as HNO_3 and HNO_2	Analysis by MIL Spec would give the following result:
99.9	0.1	99.98
99.7	0.3	99.92
99.5	0.5	99.80
99.0	1.0	99.90
84.0	16.0	97.70

It is possible to construct a similar table for the effects of NO content upon NTO assay.

It is for this reason, therefore, that a sample of NTO with 1% NO can easily meet the specification limit of 99.5% N_2O_4. Thus, the objections raised by the Rocketdyne chemists are:

a. Assay for N_2O_4 is indefinite and often erroneous.

b. Water-equivalent is inaccurate since it is based upon a vague end point and strictly empirical.

In summary, it can be said that Rocketdyne is satisfied as to the efficiency of its operators when using the MIL-P-26539A techniques, but is highly critical of the specification itself. It performs the analytical procedures described in MIL-P-26539A because of contract requirements but prefers alternate methods.

Rocketdyne later extended the Go-No Go technique to the N_2O_4 content determination when the assay was low, the rich brown color of the NTO became light and the operator could tell at a glance whether it could pass specification. Rocketdyne was satisfied with its in-house screening method but felt it was limited in use to "brown" NTO and that it could not cope readily with "green" NTO from Hercules.

ROCKET PROPULSION LABORATORY EXPERIENCE

The Air Force first noticed "green" NTO, which met the requirements of MIL-P-26539A in all respects, in the fall of 1963 in procurements from Hercules. The reaction was immediate; the material was rejected for further use until a full-scale investigation could be made. The results thereof showed that the green color was due to the presence of nitric oxide (NO) in amounts up to 1%, and not to large quantities of water, as was at first feared. In view of the fact that the effects of small quantities of NO could not be determined to be harmful, the Air Force later resumed use of this material with the proviso that it meet fully the chemical requirements of the military specification. Thus, the Air Force regards acceptance of the type of "green" NTO to be a psychological problem. Nevertheless, a supplemental data sheet for MIL-P-26539A was initiated by Edwards Air Force Base regarding the method of water analysis since NO interfered seriously with it by affecting the properties of the water-equivalent determination residue; and in addition, in December 1963 the Hercules contract was renegotiated by the Air Force Middletown Air Material Area (MAAMA). Nevertheless the experience with the "green" NTO did have the beneficial effect of exposing the weaknesses of MIL-P-26539A. On 23 March 1964, EAFB requested MAAMA to initiate a project for modification of the NTO specification. A reply is expected shortly, at which time it is expected that a program to prepare the B version of MIL-P-26539 will be started by 1 July 1964.

It is germane at this point to mention the fact that at present, under operational conditions, the Air Force limits the water content in NTO to 0.2%; this is the so-called "use limit." Thus, the Air Force, when it procures NTO at the 0.1% H_2O limit, is purchasing a grade better than it needs; by permitting the use of 0.2% level in service, it recognizes that there will be some moisture pick-up.

ROCKETDYNE EXPERIENCE

The use of NTO by Rocketdyne, in contrast to the Air Force use, is a relatively small one and often requires storage of as little as 5000 gallons for periods up to six months. The material is purchased under MIL-P-26539A and provided to the contractor. Routinely, shipments are loaded into tanks of 5000-gallon capacity and quality control samples are periodically drawn and analyzed prior to rocket engine testing and acceptance. Customarily, Rocketdyne will analyze propellants in storage tanks at least once weekly and materials on the test stand before each test firing.

Typical examples of NTO procurements to Rocketdyne are:

Vendor	Purchase Date	Amount: lbs.	gals	Color	Typical Assay
Hercules	8/15/63	36,410	$\approx$ 3000	Brown	99.8% N_2O 0.07% H_2O
Hercules	8/22/63	34,510	$\approx$ 3000	Brown	same as above
Hercules (but obtained from Marquardt)	3/24/64	2 x 1 ton cylinders		Green	99.7% N_2O_4 0.1% H_2O
Hercules	3/27/64	10,000 gallons for Reno and Santa Susanna		Green	Vendor analysis: 100.2% N_2O_4 0.06% H_2O

Rocketdyne first experienced problems at its Reno, Nevada facility on Gemini system production testing subsequent to January 1964, using NTO received from Hercules.

In the period January to March 1964, samples drawn from the NTO tanks at Santa Susanna and Reno varied in analysis, when determined both by the Go-No Go and specification techniques, such that the material fluctuated in passing or not passing the specification limits. It should be added that Rocketdyne seriously adheres to the 99.5% and 0.1% numbers and allows no leeway for adjustment, because of precision of measurement or reproducibility. Thus, although Rocketdyne admits an accuracy of no better than 0.1% in its determination of N_2O_4 by MIL-P-26539A, it will reject materials assaying 99.4% N_2O_4.

In time the Hercules material which had arrived with a brown color had started to turn green in storage. In consonance with this behavior, the water content began to analyze at the 0.2 to 0.25% level and the N_2O_4 content to fluctuate above and below the specification limit of 99.5%. The result was a situation in which the available stocks of NTO were being depleted because of rejected propellant. This condition culminated with an assay of 99.3% N_2O_4 for a 5000-gallon NTO storage tank at Santa Susanna, which coupled with similar unacceptable analyses on all available material at Santa Susanna and Reno, meant that there was no usable nitrogen tetroxide on hand for further testing.

As a result, this generalized calamity forced the Gemini, Apollo and Martin production engine programs to a halt by 22 March 1964. Upon advising McDonnell of these facts, several thousand gallons of Hercules NTO were located at the Marquardt Corporation and forwarded to Rocketdyne. This material was sampled and found to be green; this was the first time that Rocketdyne had seen fresh NTO with a green color. However, it was analyzed routinely by the methods given in MIL-P-26539A and found to be satisfactory. Further analysis confirmed the presence of 1% NO, hence the green color. In view of the analysis and lack of apprehension toward NO, the Marquardt material was fired and performed satisfactorily.

Rocketdyne then began to recognize the importance of atmospheric conditions and sampling techniques upon analytical results.

Upon re-analyzing the January 1964 shipment, it was discovered that the material now barely met specification, but was still green. Rocketdyne is satisfied that its analytical procedures are satisfactory. There then ensued a series of further analyses upon suspect propellant, both at Reno and Santa Susanna, in which the material would "slip in" and "out" of specification with an estimated reproducibility (by Rocketdyne) of 0.1%.

Because green NTO from Hercules was providing so much controversy, the Air Force Quality Assurance Representative at Rocketdyne advised that henceforth future shipments would come from Allied. Accordingly, 10 cylinders of 2000 pounds each containing NTO were received at Rocketdyne in April 1964. Table 1, which is attached as Enclosure (1), lists the inspection and acceptance data for the shipment from the vendor's plant.

Rocketdyne, however, continued further testing of the remaining cylinders and upon Go-No Go testing found that all passed the water requirement but that some failed the N_2O_4 requirement. Specification testing of this "light brown" Allied material confirmed the screening results. A complete listing follows:

No.	Date Arrive in Lab	Cylinder No.	% N_2O_4	% H_2O-equivalent	Result
1	5-5-64	A-5876	99.4	0.04	Failed
2	5-6-64	A-2750	99.5	0.04	Passed
3	5-7-64	A-886	99.4	0.03	Failed
4	5-7-64	A-2913	99.4	0.04	Failed
5	5-7-64	A-5978	99.4	0.05	Failed
6	5-8-64	A-964	99.5	0.04	Passed
7	5-8-64	A-4989	99.5	0.04	Passed
8	5-8-64	A-6810	99.5	0.04	Passed
9	5-11-64	A-1521 (Reno)	99.4	0.04	Failed
	5-19-64	*1521 (Santa Susanna	99.1	0.04	
10	5-11-64	A-1744 (Reno)	99.4	0.04	Failed
	5-19-64	*1744 (Santa Susanna	99.2	0.07	

*Repeat

As can be seen, samples Numbers 1, 3, 4, 5, 9 and 10 failed because of low N_2O_4 assay, even though these were within the admitted limits of reproducibility of the test.

These analyses were all run at least in duplicate and some in triplicate, in accordance with procedures of MIL-P-26539A. Rocketdyne reports that when NTO content is marginal, the analyses of the duplicate samples run in succession are subject to variation of a relatively large amount; when the material clearly has a good assay, then the reproducibility is excellent. Another uncontrolled variable is tank temperature fluctuation which often causes water present as nitric acid to separate out as a second phase and fall to the bottom of the tank.

Rocketdyne is very much concerned about its NTO source. Although there are sufficient stocks now on hand, the problem must arise again unless corrective actions are taken. As will be shown below, one course would be to relax the NASA use limits of NTO.

CONCLUSIONS AND RECOMMENDATIONS

There appears to be two separate and distinct types of problems associated with the use of nitrogen tetroxide as a propellant. The first of these is concerned with the appearance of green coloration in the Hercules NTO. In the case where the green derives from the presence of small quantities NO, there is no substantial evidence that it is harmful either to engine operation or performance.

There is evidence that Hercules plans to reduce the occurrence of NO in its propellant NTO. Air Force sources indicate that starting in July 1964, Hercules will provide an additional oxidation step in its process whereby the by-product NO will be quantitatively converted to N_2O_4 by oxygen and in this manner, exclude NO from its production system, according to the equation:

$$2NO + O_2 \longrightarrow N_2O_4$$

Where the green arises from excessive moisture, the problem is indeed a serious one, since this ingredient is known to be extremely corrosive above the 0.2% level. In the case of Allied product, there appears to be a contaminant present which suppresses N_2O_4 equilibrium, since the product is light brown, of a shade much lighter than the normal NTO color.

Both of these cases highlight the weaknesses of the present version of MIL-P-26539. The analysis of N_2O_4 by the current military specification, MIL-P-26539A, is considered to be inadequate as a procedure, to lack definition as a test and has proven to be a very serious handicap as a functional quality control tool for production engine testing. The Air Force is aware of the difficulties and plans to take corrective action.

As far back as December 1963, the analytical chemists of RPL were briefed by Rocketdyne on the short-comings of MIL-P-26539A and were advised that the assays for N_2O_4 and H_2O were not specific. Air Force sources state that an RFQ to industry to develop new analyses for NTO is in work and that sometime in the near future, there will be an addendum to the specification to include NO.

The question as to whether or not presence of NO in N_2O_4 is deleterious has still not been settled with finality. In the small quantities seen in the Hercules product (1% or less) the problem at the present time appears to be mainly psychological, since all the physical and chemical properties of each are indistinguishable; above this level there could be differences in vapor pressure or hypergolicity sufficient to affect ignition characteristics and pumping properties of the oxidizer.

The Air Force has sent a letter to its contractors such as, Aerojet, Martin, etc., asking what the effects of NO in N_2O_4 could be and requested guidance in this matter. No clear-cut definition has as yet been reported, and as a result the "green" NTO from Hercules has been returned to the service from which it had been removed. Such use is no longer considered to be a problem by the Air Force provided the water and N_2O_4 assay is within specification limits as modified by an EAFB supplemental data sheet of April 1964 to MAAMA modifying the water analysis so as to exclude interference from possible NO.

The question of how to analyze NO still remains open. The Pinol, California plant is working on this task and is reputed to have solved it, for levels of NO below 1.5%; the cognizant chemist (Dr. Jack Manchester) will be contacted there for further confirmation.

There appears to be a difference of opinion regarding the inclusion of NO determination in any future specification revisions. EAFB feels it is no engine problem and chooses to ignore it; Ballistics Systems Division (BSD) is concerned and is pushing to have it included in any future revisions.

It becomes germane at this point to cite the experience and practices of the Air Force relative to NTO logistics. Although NTO is procured to MIL-P-26539A, recognition is taken of future possible degradation and "aging" in storage. Therefore, a use specification is also used to guard the quality of materials going to the Air Force rocket engines. For example, in the case of the Martin Co. Transtage and others, the use limit was relaxed thereunder with no adverse effects to engine operation.

A comparison of NASA and Air Force specifications follows:

	NASA		Air Force	
	Purchase Limit	Use Limit	Purchase Limit	Use Limit
% N_2O_4	99.5	99.5	99.5	99.4
% H_2O	0.1	0.2	0.1	0.2

In view of the above and the fact that there is no segregation of NASA and Air Force stocks at Rocketdyne, there is a movement at Rocketdyne to ask for a relaxation of the NTO use limit requirements to conform to Air Force practice, details of which are contained in a forthcoming publication, Technical Order 42 B7-2-1-3.

North American Aviation considers the problem serious enough to detail a quality assurance manager (E. A. Gardner) to this area. Apparently, the crux of the problem is the fact that the model specifications for Apollo, Gemini, Transtage and G. E. engines cite MIL-P-26539A. As shown previously, the Air Force now has granted waivers for its engines, but the NASA programs still must conform to the 99.5% and 0.1% requirement for N_2O_4 and H_2O, both for procurement and use purposes. The marginal assay on delivery, the lack of provision for "aging" of propellants in storage and the inept analytical procedures of MIL-P-26539A all combine to impose a hardship on the contractor, which must adhere rigidly to the requirements imposed upon it by the engine model specifications.

With respect to performance, the following calculations obtain:

% N_2O_4	Theoretical Isp
100.0	340 sec
99.5	337.1
99.3	336.7

Thus, the difference in performance resulting in use of 99.3% N_2O_4 assay propellant vice 99.5% material is 0.4 seconds. The Air Force Plant Representative states that the accuracy of the instrumentation at the plant is no better than 5-6 seconds; obviously a difference of 0.4 seconds cannot be detected under these conditions.

In addition, the specifications for certain engines call out a requirement of a minimum performance of 285 seconds for production engines; the delivery turns out to be substantially above this (in the 291-297-second range).

Thus, a proposed set of NASA guide-lines for NTO could be

	% N_2O_4	% H_2O
For procurement and shipping	99.5	0.1
For use limits in model specification for acceptance purposes	99.4	0.2

A comparison is given with BSD Exhibit 62-118B of 5 April 1963 entitled, "Contamination Control of Titan II Fluids."

	% N_2O_4	% H_2O
Procurement	99.5	0.1
Storage in Tank	99.5	0.15
Storage in Vehicle	99.4	0.2

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Enclosure:
Table 1

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